Pergamon

Marine Pollution Bulletin Vol. 43, Nos. 1–6, pp. 93–101, 2001

Printed in Great Britain

PII: S0025-326X(01)00038-8

0025-326X/01 $ - see front matter

Persistent Organic Pollutants (POPs) in a Small, Herbivorous, Arctic Marine Zooplankton (*Calanus hyperboreus*): Trends from April to July and the Influence of Lipids and Trophic Transfer

AARON T. FISK†*, GARY A. STERN‡, KEITH A. HOBSON§††, WILLIAM J. STRACHAN‡‡, MARK D. LOEWEN‡ and ROSS J. NORSTROM†§§

†*Chemistry Department, Carleton University, Ottawa, Ont., Canada K1S 5B6*

‡*Freshwater Institute, Department of Fisheries and Oceans, Winnipeg, Man., Canada R3T 2N6*

§*Department of Biology, University of Saskatchewan, Saskatoon, Sask., Canada S7N 0W0*

††*Prairie and Northern Wildlife Research Center, CWS, Saskatoon, Sask., Canada S7N 0X4*

‡‡*National Water Research Institute, Environment Canada, Burlington, Ont., Canada L7R 4A6*

§§*National Wildlife Research Centre, Environment Canada, Hull, Que., Canada K1A 0H3*

Samples of *Calanus hyperboreus*, a herbivorous copepod, were collected ($n = 20$) between April and July 1998, and water samples ($n = 6$) were collected in May 1998, in the Northwater Polynya (NOW) to examine persistent organic pollutants (POPs) in a high Arctic marine zooplankton. Lipid content (dry weight) doubled, water content ($r^2 = 0.88$) and $\delta^{15}N$ ($r^2 = 0.54$) significantly decreased, and $\delta^{13}C$ significantly increased ($r^2 = 0.30$) in the *C. hyperboreus* over the collection period allowing an examination of the role of these variables in POP dynamics in this small pelagic zooplankton. The rank and concentrations of POP groups in *C. hyperboreus* over the entire sampling was ∑PCB (30.1 ± 4.03 ng/g, dry weight) > ∑HCH (11.8 ± 3.23) > ∑DDT (4.74 ± 0.74), ∑CHLOR (4.44 ± 1.0) > ∑ClBz (2.42 ± 0.18), although these rankings varied considerably over the summer. The α- and γ-HCH and lower chlorinated PCB congeners were the most common POPs in *C. hyperboreus*. The relationship between bioconcentration factor (BCF) and octanol–water partition coefficient (K_{ow}) observed for the *C. hyperboreus* was linear and near 1:1 (slope = 0.72) for POPs with a log K_{ow} between 3 and 6 but curvilinear when hydrophobic POPs (log $K_{ow} > 6$) were included. Concentrations of ∑HCH, ∑CHLOR and ∑ClBz increased over the sampling period, but no change in ∑PCB or ∑DDT was observed. After removing the effects of time, the variables lipid content, water content, $\delta^{15}N$ and $\delta^{13}C$ did not describe POP concentrations in *C. hyperboreus*. These results suggest that hydrophobic POP (log K_{ow} = 3.86.0) concentrations in zooplankton are likely to reflect water concentrations and that POPs do not biomagnify in *C. hyperboreus* or likely in other small, herbivorous zooplankton.

Keywords: stable isotopes; carbon-13; nitrogen-15; copepod; bioaccumulation; seasonal trends.

Introduction

Organochlorine pollutants, commonly referred to as persistent organic pollutants (POPs), have been studied intensively over the past three decades because many are persistent, bioaccumulative, toxic, and found in nearly every matrix on the planet. This is clearly the case in the Arctic, where despite limited use of these chemicals, concentrations of POPs reach high levels in upper trophic level organisms, such as polar bears (*Ursus maritimus*) (Norstrom *et al.*, 1988, 1998) and glaucous gulls (*Larus hyperboreus*) (Braune, 1994). This phenomenon occurs especially in the Arctic because of long-range transport of POPs via the atmosphere, biomagnification of POPs through the food chains, and large lipid stores in Arctic organisms (AMAP, 1998). POPs accumulate in fatty tissue due to their highly hydrophobic nature. In general, indigenous people of the

*Corresponding author. Present address: NWRI, 867 Lakeshore Road, Burlington, ONT., Canada L7R 4A6. Tel.: +1-905-336-6405; fax: +1-905-336-6430.

E-mail address: aaron.fisk@cciw.ca (A.T. Fisk).

Arctic are at greater risk to POPs than populations from more temperate regions due to the highly integrated role of wildlife for food, particularly high lipid tissues, in Arctic native society (AMAP, 1998).

Understanding the mechanisms of food chain transfer of POPs is a key component of assessing exposure to, and risk of POPs, in wildlife and humans. The majority of research on POPs in the Arctic has focused on organisms that are consumed by humans, mainly fish, birds and marine mammals. Because of this, the understanding of factors that influence POP concentrations in these organisms are much greater (see for example Hickie *et al*., 1999; Weis and Muir, 1997) than those that are not consumed by humans, such as marine zooplankton. However, concentrations at the base of food webs could have a profound influence on concentrations observed at higher trophic levels. Understanding the factors that influence concentrations in lower trophic levels will aid in understanding temporal variability in POP concentrations in various components of the Arctic and for developing fate and exposure models.

Accumulation of POPs in higher trophic level organisms is predominantly through food (trophic transfer) as opposed to water (bioconcentration). Although this is obvious for air-breathing animals it is prevalent for fish as well (Thomann and Connolly, 1984). Accumulation through food can result in concentrations in the consumer that are higher than predicted based solely on lipid–water partition ratios and greater than those in food (termed biomagnification) (Thomann and Connolly, 1984). Mechanisms, including bioconcentration or trophic transfer, and factors such as lipid content or trophic level, which influence POP concentrations in small aquatic organisms, such as zooplankton, are more poorly understood (Harding, 1986).

Calanus hyperboreus is a pelagic copepod that is very abundant and a key link in many Arctic marine food webs. *C. hyperboreus* can live 3–4 years in the Arctic (Dawson, 1978; Hirche, 1997), and have a seasonal cycle which consists of periods of dormancy at great water depths, during which breeding and egg production and release occurs, followed by periods of high feeding at shallower depths (Hirche, 1997). This cycle results in large changes in lipid content (20–50% of dry body weight) (Lee, 1974) that may influence POP dynamics.

There are few data on POP concentrations in Arctic zooplankton, due mainly to the low concentrations, and subsequent large sample size required, and the difficulty of collecting samples in the Arctic. An extensive multidisciplinary study on the Northwater Polynya (NOW) afforded the opportunity to collect sufficient samples of *C. hyperboreus* ($n = 20$) and water ($n = 6$) to examine the temporal variability of POPs in a small pelagic zooplankton from April to July during a period of high feeding and large lipid gains. Polynyas are areas of open water, often surrounded by sea ice, which can persist throughout the winter in polar seas. They are one of the most important and least understood phenomena in polar ecology (Stirling, 1980). The NOW, in northern Baffin Bay, is a high Arctic Polynya that is the largest and most productive in the Canadian Arctic. The life history strategy of *C. hyperboreus* allowed an examination of the influence of lipid content and trophic position, based on stable isotopes of nitrogen and carbon, on POP concentrations. The ratio of the heavier to lighter stable isotopes of nitrogen ($^{15}N/^{14}N$), expressed as $\delta^{15}N$, generally increases with trophic position in aquatic food chains. It provides a continuous variable with which to assess both trophic level (Michener and Schell, 1994; Hobson *et al*., 1995) and food chain transfer of POPs (Kidd *et al*., 1998). Stable-carbon isotope ratios ($^{13}C/^{12}C$) show less enrichment with trophic transfer but can be useful in evaluating sources of primary production in marine systems as well as general patterns of inshore/benthic vs. offshore/pelagic feeding preferences (Hobson and Welch, 1992; Lawson and Hobson, 2000).

Methods

Sample collection

As part of a larger study, *C. hyperboreus* were collected from numerous stations throughout the Northwater Polynya (Fig. 1) in April, May, June and July of 1998. Zooplankton samples were collected with vertical tows of zooplankton nets (1 m^2, 200 or 520 μm mesh), generally from bottom-to-surface, from the deck of the research vessel *Pierre Radisson*. Samples from the nets were immediately transferred to clean seawater. *C. hyperboreus* were sorted and separated shortly after collection (<2 h), placed in plastic cyro-vials and frozen until analysed for stable isotope analysis (SIA) and/or POPs. Samples were split for SIA and POPs analysis. SIA was performed on each sample from a station. Due to small sample sizes and low POP concentrations, samples were combined for contaminant analysis. Samples that were combined came from stations that

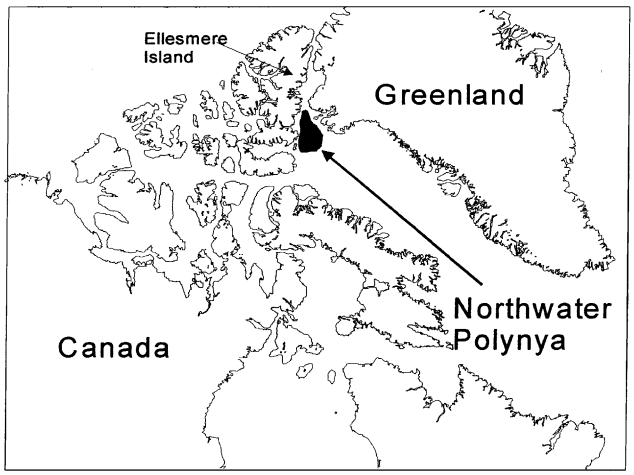

Fig. 1 Location of the Northwater Polynya and its approximate size in May/June.

were geographically close (within ~10 km) and collected within 3–4 days of each other. A total of 20 samples were analysed for POPs. Stable isotope values for the POP samples reflected the SI values and the proportion of the total mass of the POP sample of each individual sample that contributed to the larger POP sample.

Two water samples (~80 l each) were collected in May at each of three locations where *C. hyperboreus* had also been collected. Water was pumped from 2 m below the surface with a submersible pump into 40 l stainless steel cans on the deck of the ship. These cans were solvent washed (acetone and hexane) prior to collection, and were sealed until extracted. Samples were collected at the bow of the ship and the ship was positioned into the prevailing water current to minimize contamination.

Chemicals and standards

All solvents (pesticide grade) and sodium sulfate (Na_2SO_4) were obtained from BDH (Toronto, Ont., Canada). Pesticide grade Florisil, 60–100 mesh was obtained from the Floridin Corp. (Berkeley Spring, WV, USA). Biobeads SX-3 used in the GPC column was purchased from Analytical Biochemistry Laboratories (Columbia, MO, USA).

Extraction, cleanup and analysis of samples for POPs

For *C. hyperboreus*, samples were freeze dried, spiked with an internal standard (2,4,6-trichlorobiphenyl (PCB30) and octachloronapthalene) and extracted with dichloromethane (DCM)/hexane (1:1) using a Dionex ASE 200 (Dionex Canada Ltd., Oakville, Ont., Canada) accelerated solvent extractor. A fraction of the extract was used to determine lipids gravimetrically. Lipids were removed from the sample by gel permeation chromatography (GPC). The lipid-free eluate, containing the POPs, was evaporated to 1 ml and applied to a Florisil column (8 g, 1.2% deactivated). The POPs were recovered by consecutive elution with 35 ml hexane (Fraction 1 (F1)) and 38 ml of 85% hexane: 15% DCM (F2). F1 contained 90% of the chlorobenzenes, 75% of trans-nonachlor, 50% of the *o,p*-DDE and *o,p*-DDT, 15% of the *p,p*-DDT, 95% of the *p,p*-DDE, and 100% of the PCBs. F2 contained 5% of *p,p*-DDE, 10% of the chlorobenzenes, 25% of *trans*-nonachlor, 50% *o,p*-DDT and *o,p*-DDE, 90% of *p,p*-DDT, and 100% of α-hexachlorocyclohexane (HCH), β-HCH, oxychlordane, *trans*-chlordane, *cis*-chlordane, *o,p*-DDD, *p,p*-DDD and *cis*-nonachlor. All fractions were roto-evaporated, transferred to 2,2,4-trimethyl pentane and were evaporated to approximately 100 µl. Aldrin was added as a volume corrector. Samples (100 µl) were analysed on a Varian 3600 gas chromatograph (GC) equipped with a 60 m × 0.25 mm DB-5 column (J & W Scientific) and a ^{63}Ni-electron capture detector (ECD). The carrier gas was H_2 and N_2 was used as the make-up gas for the ECD. External standards were run after every six samples.

POPs were extracted from the water samples on the ship. Each sample consisted of ~80 l (two 40 l stainless steel cans). Equal amounts of a recovery standard (PCB 30) were spiked into each stainless steel can and stirred with a stainless steel rod prior to extraction. Water was pumped through oven-baked filters and then extracted with XAD-2 resin. The XAD-2 resin was kept at 2°C until analysed back at the lab. POPs were extracted from the resin using a Soxhlet extractor with methanol and DCM. The methanol and DCM were exchanged with hexane and cleaned up and fractionated on silica gel and analysed. Samples were analysed on a dual column (DB1 and DB5), single injection gas chromatograph with and ECD detector. The baselines for the chromatographs were identified manually and the areas compared with external standards.

Stable isotope analysis

Prior to stable isotope analyses, all tissue samples were washed in distilled water and then freeze dried, powdered and treated with a 2:1 chloroform:methanol solution to remove lipids. Samples were then dried under a fume hood, soaked in 0.1 N HCl to remove carbonates and allowed to dry without rinsing. Stable-carbon and nitrogen isotope assays were performed on 1 mg subsamples of homogenized materials by loading into tin cups and combusting at 1800°C in a Robo-Prep elemental analyser. Resultant CO_2 and N_2 gases were then analysed using an interfaced Europa 20:20 continuous-flow isotope ratio mass spectrometer (CFIRMS) with every five unknowns separated by two laboratory standards. Stable isotope abundances were expressed in δ notation as the deviation from standards in parts per thousand (‰) according to the following equation:

$$\delta X = [(R_{\text{sample}}/R_{\text{standard}}) - 1] \times 1000, \quad (1)$$

where X is ^{13}C or ^{15}N and R is the corresponding ratio $^{13}C/^{12}C$ or $^{15}N/^{14}N$. The R_{standard} values were based on the PeeDee Belemnite (PDB) for ^{13}C and atmospheric N_2 (AIR) for ^{15}N. Replicate measurements of internal laboratory standards (albumen) indicate measurement errors of ±0.1‰ and ±0.3‰ for stable-nitrogen isotope measurements respectively.

Statistical analysis

Concentration data was log transformed prior to statistical analysis to reduce skewness. Variation in the contaminant data was examined at the $\sum$POP group level. Individual compounds that were included in each of these groups are summarized in Table 1. The influence of five variables (water content, lipid content, collection date, δ^{15}N and δ^{13}C) on concentrations were examined using the general linear model

$$\log_e \text{concentration} = \mu + \text{water} + \text{lipid} + \text{date} + \delta^{15}\text{N} + \delta^{13}\text{C} + \varepsilon,$$

TABLE 1

Proximate composition and concentrations (mean ± 1 S.E.) of lipid and persistent organic pollutants in *Calanus hyperboreus* (ng/g, dry weight) and water (ng/l) by month collected from the Northwater Polynya.

Month	*N*	Lipid% [a]	Water%	∑ClBz[b]	∑HCH[c]	∑CHLOR[d]	∑DDT[e]	∑PCB[f]
Calanus hyperboreus								
April	1	19.1	90.97	1.23	1.04	0.21	2.36	15.66
May	5	23.4 ± 2.6	88.64 ± 1.42	2.24 ± 0.33	1.79 ± 0.33	1.0 ± 0.33	2.97 ± 0.34	29.6 ± 6.62
June	9	37.4 ± 1.8	82.59 ± 1.04	2.36 ± 0.21	7.68 ± 2.62	4.93 ± 1.77	4.95 ± 1.51	33.8 ± 8.20
July	5	42.6 ± 1.4	76.62 ± 0.67	2.95 ± 0.48	31.3 ± 6.30	7.83 ± 1.14	6.62 ± 0.52	27.2 ± 2.17
Total	20	39.3 ± 2.1	83.03 ± 1.21	2.42 ± 0.18	11.8 ± 3.23	4.44 ± 1.0	4.74 ± 0.74	30.2 ± 4.03
Water								
May	6	–	–	0.024 ± 0.001	1.2 ± 0.08	0.015 ± 0.002	0.009 ± 0.004	0.34 ± 0.08

[a] Lipid% is dry weight.
[b] ∑ ClBz (chlorobenzene) = sum of 1,2,4,5-triClBz, 1,2,3,4-triClBz, pentaClBz and hexaClBz.
[c] ∑ HCH (hexachlorocyclohexane) = sum of α-HCH, β-HCH and γ-HCH.
[d] ∑ CHLOR (chlordanes) = sum of heptachlor, heptachlor epoxide, *cis*-chlordane, *trans*-chlordane, *cis*-nonachlor, *trans*-nonachlor, and oxychlordane.
[e] ∑ DDT = sum of *p,p′*-DDD, *o,p*-DDD, *p,p′*-DDE, *o,p*-DDE, *p,p′*-DDT and *o,p*-DDT.
[f] PCB = sum of congeners 1, 3, 4/10, 7, 6, 8/5, 19, 18, 17, 24/27, 16/32, 26, 25, 31, 28, 33, 22, 45, 46, 52, 49, 47, 48, 44, 42, 41/71, 64, 40, 74, 70/76, 95/66, 56/60, 91, 84/89, 101, 99, 83, 97, 87, 85, 136, 110, 82, 151, 144/135, 149, 118, 134, 114, 131, 146, 153, 132, 105, 141, 130/176, 179, 137, 138, 158, 178/129, 175, 187, 183, 128, 185, 194, 196/203, 189, 208, 195, 207, 194, 205, 206 and 209.

where μ is a constant and ε is an error term. The significance of each variable was then assessed with type III sum of squares test using SAS for windows. Relationships between bioconcentration factor (BCF) and K_{ow}, and between water content, lipid content, $\delta^{15}N$, $\delta^{13}C$ and ∑POP concentrations and collection date were performed with simple linear regression using Systat for Windows.

BCFs were determined using data for *C. hyperboreus* that were collected at the same time (May) and location as water samples. A total of five and six samples of *C. hyperboreus* and water were used for these determinations, respectively. BCFs were only determined for POPs that were found in most samples, non-detected samples were removed from the determination. BCFs were determined using the equation:

$$BCF = [C.\ hyperboreus]/[\text{water}],$$

where [*C. hyperboreus*] is the mean concentration (ng/g, lipid corrected) of the POP in *C. hyperboreus* and [water] is the mean concentration (ng/ml) of the POP in water.

Results and Discussion

Lipid, water, $\delta^{13}C$ *and* $\delta^{15}N$

The percentage of lipid (dry weight) significantly increased ($r^2 = 0.84$), and the water content decreased ($r^2 = 0.88$), over the sampling period from 23 April to 20 July in the *C. hyperboreus* (Table 1 and Fig. 2). During this time lipid content doubled on a dry weight basis and increased sixfold on a wet weight basis. Increases in the lipid burden over the summer months in Arctic *C. hyperboreus* are well documented (Conover and Siferd, 1993; Lee, 1974), and reflect preparation for dormancy and reproduction during winter (Hirche and Niehoff, 1996).

A significant increase in $\delta^{13}C$ ($r^2 = 0.30$) and decrease in $\delta^{15}N$ ($r^2 = 0.54$) was observed with time in the *C. hyperboreus* (Fig. 2). Lipids are typically more negative in $\delta^{13}C$ value compared to other tissues (DeNiro

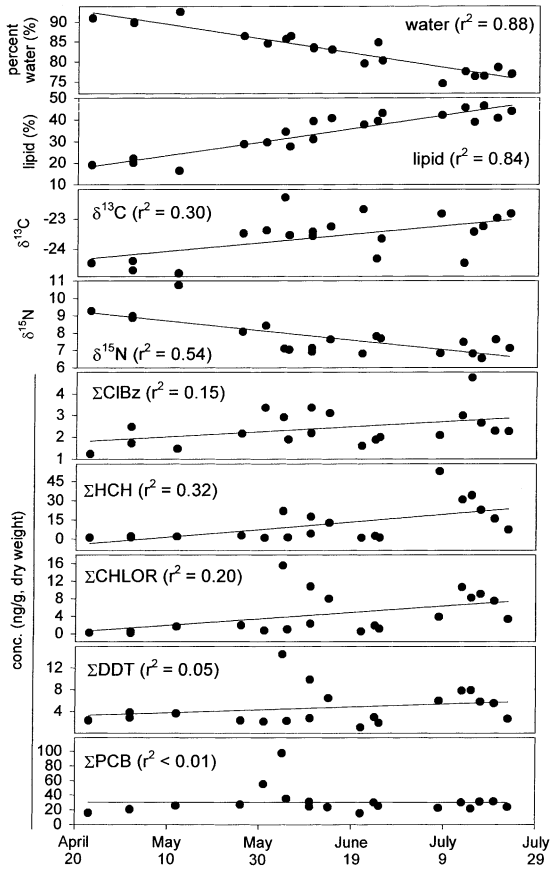

Fig. 2 Relationships between percent water, lipid percentage, $\delta^{13}C$, $\delta^{15}N$ and dry weight concentrations of ∑POP groups in *C. hyperboreus* collected from the Northwater Polynya between April and July 1998.

and Epstein, 1978) and so higher lipid content in samples would result in lower $\delta^{13}C$ values in samples. Thus, we are confident that our lipid extraction procedure was thorough and was not related to seasonal changes in copepod $\delta^{13}C$ values. *C. hyperboreus* are herbivores and changes in stable isotope signatures do not likely reflect a large change in trophic level. Increasing $\delta^{13}C$ in the *C. hyperboreus* may have reflected a change in the phytoplankton species composition (Fry, 1996) that was consumed by *C. hyperboreus* over the collection period. Fast growing diatoms have been found to have ^{13}C-rich isotopic composition that resulted in a shift to higher $\delta^{13}C$ in grazing zooplankton but with no change in trophic level (Fry and Wainright, 1991). Diatom abundance in the NOW increased over the sampling period of this study. Alternatively, if ice algal consumption increased during the study copepod $\delta^{13}C$ values would be expected to also increase since algae can be significantly enriched over phytoplankton (Hobson and Welch, 1992; Hobson *et al.*, 1995; France, 1995). This may have been the case during April and May before significant phytoplankton production in the NOW, but would have quickly diminished thereafter. Changes in $\delta^{15}N$ may reflect a change in stable isotope signatures as the *C. hyperboreus* moves from a period of dormancy and low metabolic activity in the winter to one of high feeding during the spring and early summer. During the winter *C. hyperboreus* do not feed but breed and produce eggs (Hirche and Niehoff, 1996) and therefore have to draw upon reserves. During this time, utilization of stored protein and amino acids may result in additional fractionation favoring the heavier isotope of nitrogen and leading to an increase in $\delta^{15}N$. Renewed feeding in the spring would then result in a decrease in the $\delta^{15}N$ signature in *C. hyperboreus*. Nutrient stress in birds was shown to result in an increase in $\delta^{15}N$ (Hobson and Clark, 1992), but evidence of such an effect in invertebrates is lacking.

Relative abundance and concentrations of POPs in C. hyperboreus and water

Concentrations (dry weight) of POP groups in *C. hyperboreus* are summarized in Table 1. Ranked from highest to lowest and over the entire sampling, $\sum$PCB > $\sum$HCH > $\sum$DDT, $\sum$CHLOR > $\sum$ClBz. In May, $\sum$HCH was less prominent and the relative ranking was $\sum$PCB > $\sum$DDT > $\sum$ClBz > $\sum$HCH > $\sum$CHLOR. These rankings differed in the water samples collected in May, where $\sum$HCH was the dominant POP group followed by $\sum$PCB > $\sum$ClBz > $\sum$CHLOR > $\sum$DDT. The higher prevalence of $\sum$DDT and $\sum$ClBz in *C. hyperboreus* in May compared with water likely reflects the greater bioaccumulation potential of these more hydrophobic chemicals (see below).

The most prominent individual POP in *C. hyperboreus* and water was α-HCH. PCB congener profiles in the *C. hyperboreus* and water were dominated by the lower chlorinated congeners when compared to Aroclor mixtures (Fig. 3), and in general, the most common POPs were those that were less chlorinated. Higher chlorinated PCBs, e.g., CB 180 or 206, were rarely detected. Higher chlorinated POPs are seldom observed in marine zooplankton or water, even from temperate oceans

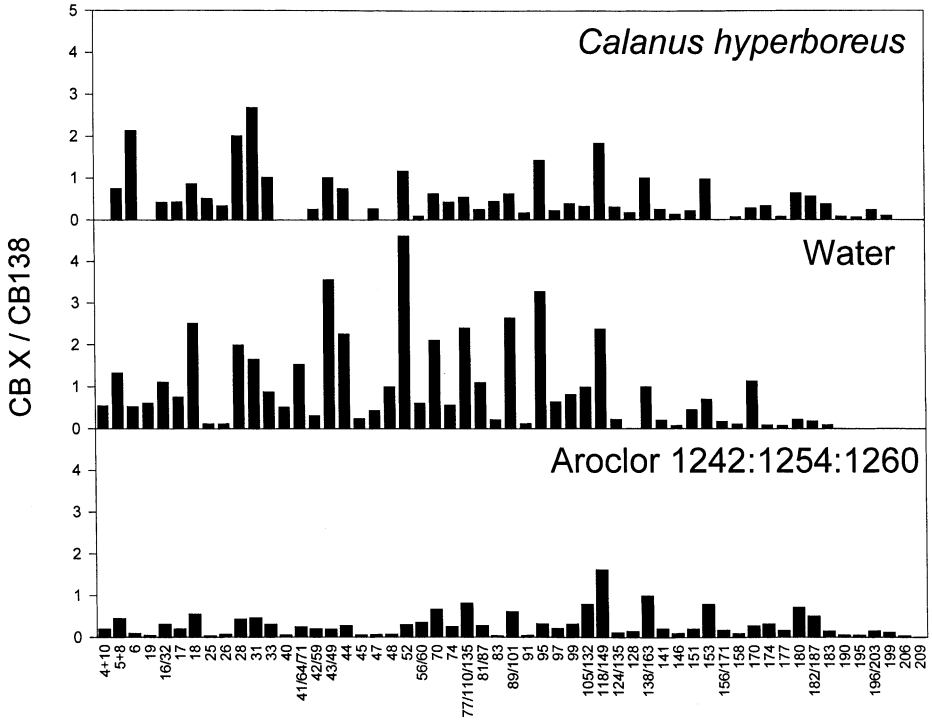

Fig. 3 Relative PCB congener (CB X/CB 138) profiles in *C. hyperboreus*, water and Aroclor 1242:1254:1260.

(Weisbrod *et al.*, 2000; Hargarve *et al.*, 2000; Harding *et al.*, 1997). Following α-HCH, the most common chemicals in *C. hyperboreus* ranked by concentration were: CB 31, CB 95/66, γ-HCH, CB 28, CB52, HClBz, CB 6, *cis*-chlordane and *p,p'*-DDE. In water, α-HCH was followed by: γ-HCH, β-HCH, CB 52, CB 43/49, CB 95/66, CB 101, CB118 and CB 18. α- and γ-HCH are generally the most common POPs measure in Arctic seawater (Hargrave *et al.*, 1997).

There are very limited data on POPs in Arctic zooplankton, particularly marine, and none for individual zooplankton species. Bidleman *et al.* (1989) reported POP concentrations for marine zooplankton, which included *C. hyperboreus* and two other species, collected under ice in the Arctic ocean in 1986 and 1987. Although lipid content and relative concentrations between POP groups varied between years in that study, concentrations were similar to those found for *C. hyperboreus* in the present study. Hargrave *et al.* (1992) reported comparable POP concentrations for mixed zooplankton (>509 μm), including *C. hyperboreus*, collected at the same time and place as those reported in Bidleman *et al.* (1989). $\sum$PCB concentrations of 12.1 ng/g (wet weight) were reported for freshwater zooplankton collected in 1993 in SE Ellesmere Island (AMAP, 1998), close to those reported in this study. All of the data reported above were collected at similar latitudes and suggest that POP concentrations in smaller pelagic marine zooplankton have not decreased significantly between the late 1980s and 1998.

Water concentrations of POPs in the NOW water were similar to concentrations reported previously for Canadian Arctic seawater, with some notable exceptions. Concentrations of $\sum$ClBz, $\sum$CHLOR and $\sum$DDT in Canadian Archipelago seawater collected in 1992 (Bidleman *et al.*, 1995) are nearly identical to those reported in this work. However, concentrations of $\sum$HCH reported for the Canadian Archipelago in 1992 (Bidleman *et al.*, 1995) and Barrow Strait in 1993 (Hargrave *et al.*, 1997) are 4–5 times higher. These results suggest minor changes in seawater concentrations of most POPs but concentrations of HCH isomers are declining, consistent with observations of data from the 1990s and 1980s (Hargrave *et al.*, 1997).

BCF–K_{ow} relationships

It has been suggested that if POP concentrations in the lipid of aquatic organisms are at equilibrium with water concentrations, simple one-to-one log–linear relationships between BCF (using lipid-corrected data for the organism) and K_{ow} should be observed (Mackay, 1982). However, BCFs of very hydrophobic POPs ($\log K_{ow} > 6.0$) have been shown to deviate below this 1:1 relationship in laboratory experiments (Gobas *et al.*, 1989; Fox *et al.*, 1994) and field measurements (Bremle *et al.*, 1995). An analysis of a large data set of BCF values found that the BCF–K_{ow} relationship was linear for POPs with a $\log K_{ow}$ range of 3–6, but that a curvilinear model provides a stronger fit when very hydrophobic chemicals were included (Devillers *et al.*, 1996). The BCF–K_{ow} relationship observed for the *C. hyperboreus* in this work was linear, and near 1:1, for POPs with a $\log K_{ow}$ between 3 and 6 but curvilinear when all POPs were included (Fig. 4), consistent with the previously reported relationships. Hargarve *et al.* (2000), using POPs with a $\log K_{ow}$ range of 3.85–6.53, reported $\log$BCF–$\log K_{ow}$ slopes for Arctic marcozooplankton ($b = 0.61$–0.97) that were very similar to the slope reported in this study ($b = 0.72$, Fig. 4).

The curvilinear phenomenon observed for the BCF–K_{ow} relationships has been attributed to a number of factors including overestimation of bioavailable water concentrations (Gobas *et al.*, 1989), inaccurate K_{ow}s (Chiou, 1985), octanol being a poor surrogate for lipids (Chessell *et al.*, 1992) elimination into feces (Gobas *et al.*, 1989) and/or insufficient time to reach equilibrium (Hawker and Connell, 1985). Most of these variables cannot be assessed in this study but there is evidence that the *C. hyperboreus* have not achieved equilibrium with the water due to the rapid increase in lipid in the *C. hyperboreus* over the collection period. Laboratory depuration-experiments with marine copepods have found the half-lives of hydrophobic POPs (such as DDT $\log K_{ow} = 6.19$ (Mackay *et al.*, 1989)) to be >10 days (Harding and Vass, 1979). Such a half-life would require greater than 20 days to approach equilibrium. The time

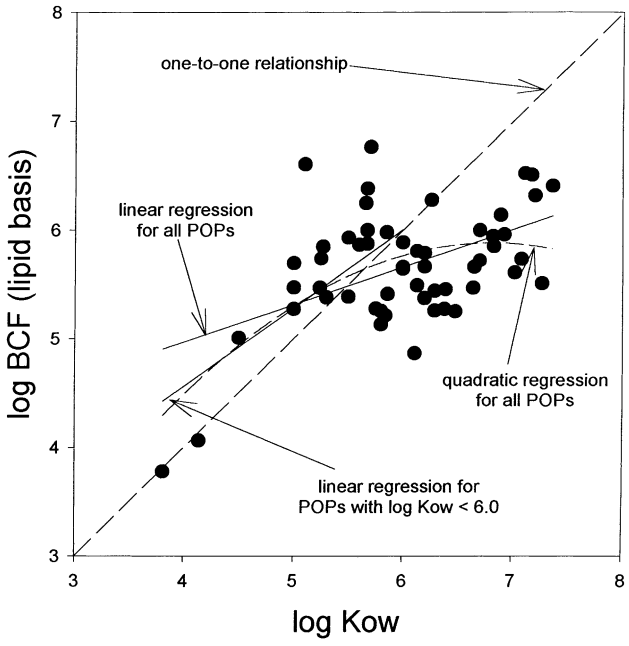

Fig. 4 Log BCF–$\log K_{ow}$ relationships for *C. hyperboreus* collected in May. BCF = [*C. hyperboreus*, lipid weight, $n = 5$]/[water, $n = 6$]. The dash line represents a 1:1 relationship between $\log$BCF and $\log K_{ow}$. Linear regression for all POPs ($\log \text{BCF} = 3.6 + (0.35 \log K_{ow})$, $r^2 = 0.25$, $p < 0.001$) and for POPs with a $\log K_{ow} < 6.0$ ($\log \text{BCF} = 1.7 + (0.72 \log K_{ow})$, $r^2 = 0.39$, $p < 0.01$) are solid lines identified on the graph. Quadratic regression for all POPs ($\log \text{BCF} = -2.3 + (2.4 \log K_{ow}) - (0.2 \log K_{ow}^2)$, $r^2 = 0.32$, $p < 0.001$) is the dash line.

required for a *Calanus* spp to come to equilibrium with water concentrations of DDT in laboratory experiments at 6°C was reported to be 3–4 weeks (Darrow and Harding, 1975). Cold temperatures slow the kinetics of POPs (Nawaz and Kirk, 1995), so the time to equilibrium in the cold waters of the NOW would likely be even slower (Harding and Addison, 1986). Therefore, very hydrophobic POP concentrations may not reach equilibrium between *C. hyperboreus* and water if lipid levels were increasing in *C. hyperboreus*. As well, if water concentrations of the POPs change seasonally, which is observed in the Arctic (Hargrave *et al.*, 1997), than the slow kinetics of very hydrophobic POPs may mean that zooplankton never achieve equilibrium with water. Conversely, during winter, as lipids decline in *C. hyperboreus*, BCFs would likely be greater than their corresponding K_{ow} values for these very hydrophobic POPs. In this case, high BCFs could be misinterpreted as being caused by trophic transfer or biomagnification.

An alternative explanation for the lower than expected BCFs for the very hydrophobic POPs could be that surface waters collected over-estimate POP concentrations that the *C. hyperboreus* were exposed. The water analysed was collected at the surface and zooplankton were collected by bottom to surface net tows. Concentrations of some free dissolved POPs decline with depth (Harner *et al.*, 1999). If the *C. hyperboreus* were exposed at depth to lower concentrations of POPs then the decline in the BCF–K_{ow} relationship that we observed would be expected.

Log BCFs of POPs that are substantially higher than those predicted by $\log K_{ow}$ have been shown to be due to trophic transfer, i.e., dietary accumulation (Thomann *et al.*, 1992). Because of this, BCF is not a good predictor of hydrophobic POP concentrations in aquatic organisms for which dietary accumulation results in biomagnification (Oliver and Niimi, 1985). The near 1:1 relationship observed for BCF–K_{ow} (slope = 0.74) for POPs in *C. hyperboreus* in the range of $\log K_{ow}$ between 3.8 and 6.0 (Fig. 4) suggest that POPs do not biomagnify in small herbivorous zooplankton. Kwano *et al.* (1986) found 1:1 relationships between BCF and K_{ow} for chlordane compounds ($\log K_{ow}$s in the range 5–6) in the North Pacific zooplankton and concluded that zooplankton concentrations were governed by seawater concentrations. Near 1:1 relationships were observed between log BCF (reported as BAFs but calculated as concentration in zooplankton over water) and $\log K_{ow}$ for POPs ($\log K_{ow}$ range of 3.86–6.53) in Arctic zooplankton (Hargarve *et al.*, 2000). Hargrave *et al.* (1992) concluded that biomagnification was not occurring in zooplankton based on the fact that POP concentration in Arctic zooplankton were similar to particulate matter and did not increase with zooplankton size. Concentrations of $\sum$PCBs were lower in copepods than in diatoms, potentially due to metabolism in the copepod, in samples collected in the Baltic Sea (Kannan *et al.*, 1995).

The suggestion that POPs do not biomagnify significantly in small pelagic zooplankton does not suggest that trophic transfer was not occurring in these organisms. Lab experiments have shown that small marine zooplankton efficiently assimilate POPs from water and food (Harding and Vass, 1979; Harding *et al.*, 1981). In the ocean, zooplankton likely accumulate POPs from both water and food. The reason that BCFs were not greater than K_{ow} in zooplankton, but are in larger organisms such as fish is likely due to body size and relative trophic position. Smaller organisms have a greater respiratory surface to body weight ratio (Harding and Addison, 1986), which would increase their ability to both accumulate POPs from and eliminate to water. Elimination rates of POPs in aquatic organisms are inversely rated to body size (Fisk *et al.*, 1998), even for different size class of invertebrates (Landrum, 1988). Fish do not eliminate POPs, with $\log K_{ow}$s > 3, quickly enough to compensate for accumulation through trophic transfer. Therefore, BCFs are higher than K_{ow} in fish because equilibrium with the surrounding water is not achieved. Hydrophobic POPs have been shown to increase in concentrations with trophic level in aquatic food chains (Kidd *et al.*, 1998), and the greater the trophic level of an organism the higher its POP concentration (Rasmussen *et al.*, 1990). Therefore, the discrepancy between hydrophobic POP concentrations in food and water is much smaller for *C. hyperboreus*, a second trophic level organism, than for higher trophic level organisms.

Relationships with stable isotopes and seasonal trends

ANOVA, using type III sum-of-squares, found that water content, lipid content, date, δ^{15}N and δ^{13}C were not significant variables describing POP concentrations in *C. hyperboreus*. Type III sum-of-squares examines the influence of a variable after removing the variability associated with all other variables. Using type I sum-of-squares, which assigns variability to variables in the order in that they are placed in the model, found that water content, lipid content or date, whichever variable was placed in the model first, significantly described the concentrations of $\sum$ClBz, $\sum$HCH and $\sum$CHLOR. No variables significantly described $\sum$DDT and $\sum$PCB concentrations. Dry weight concentrations of $\sum$ClBz, $\sum$HCH and $\sum$CHLOR increased over the sampling period, although there was a large amount of variability (Fig. 2). Lipid weight concentrations of $\sum$HCH and $\sum$CHLOR increased with time, and lipid weight concentrations of $\sum$ClBz decreased with time. $\sum$DDT concentrations, dry or lipid weight, and dry weight concentrations of $\sum$PCB were not significantly related to time. Lipid weight concentrations of $\sum$PCB significantly declined with time. The fact that lipid and δ^{15}N, and δ^{13}C and water content, failed to describe a significant amount of the variability in POP concentrations provides further evidence that water concentrations are the determining factor in concentrations of POPs in

small herbivorous marine zooplankton. It also suggests that changes in lipid content and $\delta^{15}N$ may not provide useful information on POP concentrations in these organisms.

Values of $\delta^{15}N$ have been shown to be positively correlated with lipid concentrations of POPs in aquatic food webs (Fisk *et al*., 2001; Kidd *et al*., 1998), although demonstration of this phenomenon in an individual species is lacking. The decrease in $\delta^{15}N$ observed in the *C. hyperboreus* should have resulted in a decrease in POP concentrations. This was observed for lipid corrected concentrations of $\sum$ClBz and $\sum$PCB, although these relationships were weak, but was not observed for $\sum$DDT, $\sum$CHLOR or $\sum$HCH. Although the increase in lipid observed in the *C. hyperboreus* might have confounded these relationships, $\delta^{15}N$ values have been shown to be correlated to POP concentration above and beyond the effects of lipid (Kidd *et al*., 1998). The lack of strong relationships between POP concentrations and $\delta^{15}N$ may be due to the fact that seasonal changes in copepod $\delta^{15}N$ values do not reflect trophic level changes but rather metabolic changes in *C. hyperboreus*. Such metabolic changes should be independent of POP kinetics.

The evidence that water is the over riding factor controlling zooplankton POP concentrations suggests that because there were changes in $\sum$ClBz, $\sum$HCH and $\sum$CHLOR concentrations in *C. hyperboreus* over the sampling period that concentrations of these POPs in the NOW water also changed. No changes in $\sum$DDT or $\sum$PCB were observed in the *C. hyperboreus*. Seasonal trends in water concentrations of POPs in the NOW are not available. Evidence that changes in zooplankton POP concentrations mirror those in water have been observed in other studies. Lipid concentrations of α-HCH and $\sum$PCB increased 4.2 fold and remained the same, respectively, between May and August 1986 in Arctic marine zooplankton (Hargrave *et al*., 1992), which was similar to those observed for lipid concentrations in this report. Hargarve *et al*. (2000) reported that POP concentrations decreased in Arctic zooplankton over the onset of open water consistent with deceases in water concentrations of these POPs. Changes in lipid concentrations of $\sum$ClBz, $\sum$HCH and $\sum$CHLOR observed in the NOW *C. hyperboreus* could be due to changes in the relative source of waters in the NOW. The contribution of water from Baffin Bay and Arctic Ocean (via the Kane Basin) increased and decreased, respectively, over the sampling period. Hargarve *et al*. (2000) suggested that increases in suspended particulate matter resulted in decreased bioavailable water concentrations of POPs. Biological production increased in the NOW over the sampling period used in this study and may have influenced the POP concentrations observed in *C. hyperboreus*.

Funding for this project was provided in part by an Natural Science and Engineering Research Council (NSERC) Network grant on the Northwater Polynya, Canadian Wildlife Service, Polar Continental Shelf Project and the National Science Foundation (NSF grant to George Hunt Jr.). The authors would like to thank the many scientists of the NOW project, especially Nina Karnovsky, Meike Holst, Ian Stirling, Dennis Andriashek, Nick Lunn, George Hunt, Martin Fortier, Marc Ringette and Louis Fortier. We thank Patricia Healy for assistance with sample preparation. Garth Parry, University of Saskatchewan performed stable isotope analyses. We thank the HTA of Grise Fjord for granting us permission to collect samples in their area. Barry Hargrave and Gareth Harding (Bedford Institute of Oceanography) provided insightful comments on an earlier draft. This project would not have been possible without the dedicated and skillful assistance of the *Pierre Radisson* Coast Guard captains and crew.

AMAP (1998) AMAP Assessment Report: Arctic Pollution Issues. Arctic Monitoring and Assessment Programme (AMAP), Oslo, Norway, pp. xii + 859.

Bidleman, T. F., Patton, G. W., Walla, M. D., Hargrave, B. T., Vass, W. P., Erickson, P., Fowler, B., Scott V., and Gregor, D. J. (1989) Toxaphene and other organochlorines in Arctic ocean fauna: Evidence for atmospheric delivery. *Arctic* **42**, 307–313.

Bidleman, T. F., Jantunen, L. M., Falconer, R. L., Barrie, L. A., and Fellin, P. (1995) Decline of hexachlorocyclohexanes in the Arctic atmosphere and reversal of air–sea gas exchange. *Geophysical Research Letters* **22**, 219–222.

Braune, B. M. (1994) Trends and effects of environmental contaminants in Arctic seabirds, waterfowl, and other wildlife. I. Contaminants in waterfowl: Native harvest in NWT. In *Synopsis of Research Conducted under the 1993/1994 Northern Contaminants Program, Indian and Northern Affairs Canada, Environmental Studies 72, Ottawa* eds. J. L. Murray, and R. G. Shearer, pp. 305–311.

Bremle, G., Okla, L., and Larsson, P. (1995) Uptake of PCBs in fish in a contaminated river system: Bioconcentration factors measured in the field. *Environmental Science and Technology* **29**, 2010–2015.

Chessell, M., Hawker, D. W., and Connell, D. W. (1992) Influence of solubility in lipid on bioconcentration of hydrophobic compounds. *Ecotoxicology and Environmental Safety* **23**, 260–273.

Chiou, C. T. (1985) Partition coefficents of organic compounds in lipid-water systems and correlations with fish bioconcentration factors. *Environmental Science and Technology* **19**, 57–62.

Conover, R. J., and Siferd, T. D. (1993) Dark-season survival strategies of coastal zone zooplankton in the Canadian Arctic. *Arctic* **46**, 303–311.

Darrow, D. C., and Harding, G. C. H. (1975) Accumulation and apparent absence of DDT metabolism by marine copepods, *Calanus* spp., in culture. *Journal of the Fisheries Research Board of Canada* **32** 1845–1849.

Dawson, J. K. (1978) Vertical distribution of *Calanus hyperboreus* in the central Arctic ocean. *Limnology and Oceanography* **23**, 950–957.

DeNiro, M. J., and Epstein, S. (1978) Influence of diet on the distribution of carbon isotopes in animals. *Geochimica Cosmochimica Acta* **42**, 495–506.

Devillers, J., Bintein, S., and Domine, D. (1996) Comparison of BCF models based on log*P*. *Chemosphere* **33**, 1047–1065.

Fisk, A. T., Hobson, K. A., and Norstrom, R. J. (2001) Influence of chemical and biological factors on trophic transfer of persistent organic pollutants in the Northwater Polynya marine food web. *Environmental Science and Technology*, in press.

Fisk, A. T., Norstrom, R. J., Cymbalisty, C. D., and Muir, D. C. G. (1998) Dietary accumulation and depuration of hydrophobic organochlorines: Bioaccumulation parameters and their relationship with the octanol/water partition coefficient. *Environmental Toxicology and Chemistry* **17**, 951–961.

Fox, K., Zauke, G., and Butte, W. (1994) Kinetics of bioconcentration and clearance of 28 polychlorinated biphenyl congeners in zebrafish (*Brachydanio rerio*). *Ecotoxicology and Environment Safety* **28**, 99–109.

France, R. L. (1995) Carbon-13 enrichment in benthic compared to planktonic algae: foodweb implications. *Marine Ecology Progress Series* **124**, 307–312.

Fry, B. (1996) $^{13}C/^{12}C$ fractionation by marine diatoms. *Marine Ecology and Progress Series* **134**, 283–294.

Fry, B., and Wainright, S. C. (1991) Diatom sources of ^{13}C-rich carbon in marine food webs. *Marine Ecology and Progress Series* **76**, 149–157.

Gobas, F. A. P. C., Clark, K. E., Shiu, W. Y., and Mackay, D. (1989) Bioconcentration of polybrominated benzenes and biphenyls and related superhydrophobic chemicals in fish: Role of bioavailability and elimination into feces. *Environmental Toxicology and Chemistry* **8**, 231–245.

Harding, G. C. (1986). Organochlorine dynamics between zooplankton and their environment, a reassessment. *Marine Ecology and Progress Series* **33**, 167–191.

Harding, G. C., and Addison, R. F. (1986) Accumulation and effects of PCBs in marine invertebrates and vertebrates. In *PCBs and the Environment, Volume II* ed. J. S. Waid, pp. 9–30. CRC Press, Boca Raton, FL.

Harding, G. C. H., and Vass, W. P. (1979) Uptake and seawater and clearance of *p,p′*-DDT by marine planktonic crustacea. *Journal of the Fisheries and Research Board of Canada* **36**, 247–254.

Harding, G. C., Vass, W. P., and Drinkwater, K. F. (1981) Importance of feeding, direct uptake from seawater, and transfer from generation to generation in the accumulation of an organochlorine (*p,p′*-DDT) by the marine planktonic copepod *Calanus finmarchicus*. *Canadian Journal of Fisheries and Aquatic Science* **38**, 101–119.

Harding, G. C., LeBlanc, R. J., Vass, W. P., Addison, R. F., Hargave, B. T., Pearre Jr. S., Dupuis, A., and Brodie, P. F., 1997. Bioaccumulation of polychlorinated biphenyls (PCBs) in the marine pelagic food web, based on a seasonal study in the southern Gulf of St. Lawrence, 1976–1977. *Marine Chemistry* **56**, 145–179.

Hargrave, B. T., Harding, G. C., Vass, W. P., Erickson, P. E., Fowler, B. R., and Scott, V. (1992) Organochlorine pesticides and polychlorinated biphenyls in the Arctic Ocean food web. *Archives of Environmental Contamination and Toxicology* **22**, 41–54.

Hargrave, B. T., Barrie, L. A., Bidleman, T. F., and Welch, H. E. (1997) Seasonality in exchange of organochlorines between Arctic air and seawater. *Environmental Science and Technology* **31**, 3258–3266.

Hargarve, B. T., Phillips, G. A., Vass, W. P., Bruecker, P., Welch, H. E., and Siferd, T. D. (2000) Seasonality in bioaccumulation of organochlorines in lower trophic level Arctic marine biota. *Environmental Science and Technology* **34**, 980–987.

Harner, T., Kylin, H., Bidleman, T. F., and Strachan, W. M. J. (1999) Removal of a- and g-hexachlorocyclohexane and enantiomers of a-hexachlorocyclohexane in the eastern Arctic Ocean. *Environmental Science and Technology* **33**, 1157–1164.

Hawker, D. W., and Connell, D. W. (1985) Relationships between partition coefficient, uptake rate constant, clearance rate constant and time to equilibrium for bioaccumulation. *Chemosphere* **14**, 1205–1219.

Hickie, B. E., Mackay, D., and de Koning, J. (1999) Lifetime pharmacokinetic model for hydrophobic contaminants in marine mammals. *Environmental Toxicology and Chemistry* **18**, 2622–2633.

Hirche, H.-J. (1997) Life cycle of the copepod *Calanus hyperboreus* in the Greenland Sea. *Marine Biology* **128**, 607–618.

Hirche, H.-J., and Niehoff, B. (1996) Reproduction of the Arctic copepod *Calanus hyperboreus* in the Greenland Sea-field and laboratory observations. *Polar Biology* **16**, 209–219.

Hobson, K. A., and Clark, R. G. (1992) Assessing avian diets using stable isotopes II: Factors influencing diet-tissue fractionation. *Condor* **94**, 189–197.

Hobson, K. A., and Welch, H. E. (1992) Determination of trophic relationships within a high Arctic marine food web using stable-isotope analysis. *Marine Ecology Progress Series* **84**, 9–18.

Hobson, K. A., Ambrose, Jr. W. G., and Renaud, P. E. (1995) Sources of primary production, benthic–pelagic coupling, and trophic relationships within the Northeast water polynya: Insights from $\delta^{13}C$ and $\delta^{15}N$ analysis. *Marine Ecology and Progress Series* **128**, 1–10.

Kannan, N., Reusch, T. B. H., Schulz-Bull, D. E., Petrick, G., and Duinker, J. C. (1995) Chlorobiphenyls: Model compounds for metaboism in food chain organisms and their potential use as ecotoxicological stress indicators by application of the metabolic slope concept. *Environmental Science and Technology* **29**, 1851–1859.

Kidd, K. A., Hesselein, R. H., Ross, B. J., Koczanski, K., Stephens, G. R., and Muir, D. C. G. (1998) Bioaccumulation of organochlorines through a remote freshwater food web in the Canadian Arctic. *Environmental Pollution* **102**, 91–103.

Kwano, M., Matsushita, S., Inoue, T., Tanaka, H., and Tatsukawa, R. (1986) Biological accumulation of chlordane compounds in marine organisms. *Marine Pollution Bulletin* **17**, 512–516.

Landrum, P. F. (1988) Toxicokinetics of organic xenobiotics in the amphipod, *Pontoporeia hoyi*: Role of physiological and environmental variables. *Aquatic Toxicology* **12**, 245–271.

Lawson, J. W., and Hobson, K. A. (2000) Diet of harp seals (*Pagophilus groenlandicus*) in nearshore northeast Newfoundland: Inferences from stable-carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) isotope analysis. *Marine Mammal Science* **16**, 578–591.

Lee, R. F. (1974) Lipid composition of the copepod *Calanus hyperboreus* from the Arctic Ocean. Changes with depth and season. *Marine Biology* **26**, 313–318.

Mackay, D. M. (1982) Correlation of bioconcentration factors. *Environmental Science and Technology* **16**, 274–278.

Mackay, D., Shiu, W.-Y., and Ma, K.-C. (1989) *Physical–Chemical Properties and Environmental Handbook*. CRC Press, Boca Raton, FL.

Michener, R. H., and Schell, D. M. (1994) Stable isotope ratios as tracers in marine and aquatic food webs. In *Stable Isotopes in Ecology and Environmental Science*, eds. K. Lajtha and R. H. Michener, pp. 138–157. Blackwell Scientific, Oxford.

Nawaz, S., and Kirk, K. L. (1995) Temperature effect on bioconcentration of DDE by *Daphnia*. *Freshwater Biology* **34**, 173–178.

Norstrom, R. J., Belikov, S. E., Born, E. W., Garner, G. W., Malone, B., Olpinski, M. A., Ramsay, M. A., Schliebe, S., Stirling, I., Stichov, M. S., Taylor, M. K., and Wiig, O. (1998) Chlorinated hydrocarbon contaminants in polar bears from eastern Russia, North America, Greenland, and Svalbard: biomonitoring of Arctic pollution. *Archives of Environmental Contamination and Toxicology* **35**, 354–367.

Norstrom, R. J., Simon, M., Muir, D. C. G., and Schweinsburg, R. E. (1988) Organochlorine contaminants in arctic marine food chains: identification, geographical distribution, and temporal trends in polar bears. *Environmental Science Technology* **22**, 1063–1071.

Oliver, B. G., and Niimi, A. J. (1985) Bioconcentration factors of so me halogenated organics in rainbow trout: Limitations in their use for prediction of environmental residues. *Environmental Science and Technology* **19**, 842–849.

Stirling, I. (1980) The biological importance of Polynyas in the Canadian Arctic. *Arctic* **33**, 305–315.

Thomann, R. V., and Connolly, J. P. (1984) Model of PCB in the Lake Michigan lake trout food chain. *Environmental Science and Technology* **18**, 65–71.

Thomann, R. V., Connolly, J. P., and Parkerton, T. F. (1992) An equilibrium model of organic chemical accumulation in aquatic food webs with sediment interaction. *Environmental Toxicology and Chemistry* **11**, 615–629.

Weis, I. M., and Muir, D. C. G. (1997) Geographical variation of persistent organochlorine concentrations in blubber of ringed seal (*Phoca hispida*) from the Canadian Arctic: Univariate and multivariate approaches. *Environmental Pollution* **96**, 321–335.

Weisbrod, A. V., Shea, D., Moore, M. J., and Stegeman, J. J. (2000) Organochlorine exposure and bioaccumulation in the endangered Northwest Atlantic right whale (*Eubalaena glacialis*) population. *Environmental Toxicology and Chemistry* **19**, 654–666.